PATENT ABSTRACTS OF JAPAN

(11)Publication number : 05-315078
(43)Date of publication of application : 26.11.1993

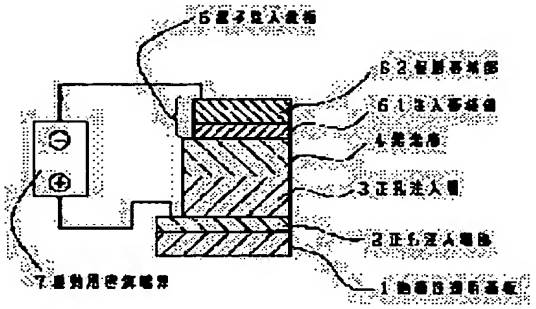
(51)Int.Cl. H05B 33/12

(21)Application number : 04-119339
(22)Date of filing : 13.05.1992

(71)Applicant : FUJI ELECTRIC CO LTD
(72)Inventor : NABETA OSAMU
KOSHO NOBORU

(54) ORGANIC THIN FILM LUMINESCENT ELEMENT

(57)Abstract:
PURPOSE: To increase stability at the time of continuously emitting light by laminating a protection band and an implantation band, in one of an electron implanting electrode or positive hole implanting electrode.
CONSTITUTION: Glass or the like is used as an insulating transparent substrate 1, and a semitransparent film of Au and ITO or the like are formed by evaporation as a positive hole implanting electrode 2, to set a film thickness to 100 to 2000Å. In a positive hole implanting layer 3, a hydrazone compound is formed at about 300 to 800Å film thickness by resistance heating method or the like. By this constitution, adhesion of an implanting band is increased by a protective band, and an electron implanting electrode can be prevented from its separation, to increase stability of a device.



LEGAL STATUS

[Date of request for examination]	03.03.1998
[Date of sending the examiner's decision of rejection]	
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	withdrawal
[Date of final disposal for application]	11.05.2000
[Patent number]	
[Date of registration]	
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] It is what it has the electrode of the couple of a hole-injection electrode and an electronic notes telegram pole, and the charge impregnation layer and luminous layer which were inserted into this electrode, and a charge impregnation layer receives impregnation of a charge from an electrode, and, subsequently to a luminous layer, carries out transport impregnation of this. It is the thing of the hole injection layer which receives impregnation of an electron hole from a hole-injection electrode, and the electronic injection layers which receive impregnation of an electron from an electronic notes telegram pole which contains a hole injection layer at least. It is the organic thin film light emitting device which a luminous layer emits light in predetermined wavelength in response to impregnation of an electron hole and an electron, and is characterized by an electronic notes telegram pole consisting of the impregnation band section and the guard-band section before long, as for the electrode of a couple.
[Claim 2] The organic thin film light emitting device characterized by the thickness of the impregnation band section being in 30 thru/or the range of 150A in an organic thin film light emitting device according to claim 1.
[Claim 3] The organic thin film light emitting device characterized by the impregnation band section consisting of a metal of 4eV or less of work functions in an organic thin film light emitting device according to claim 1.
[Claim 4] The organic thin film light emitting device characterized by the impregnation band section being a magnesium metal in an organic thin film light emitting device according to claim 3.

[Translation done.]

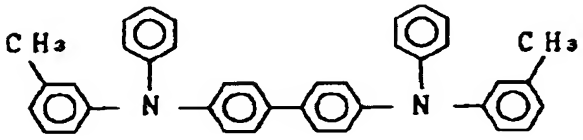
* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

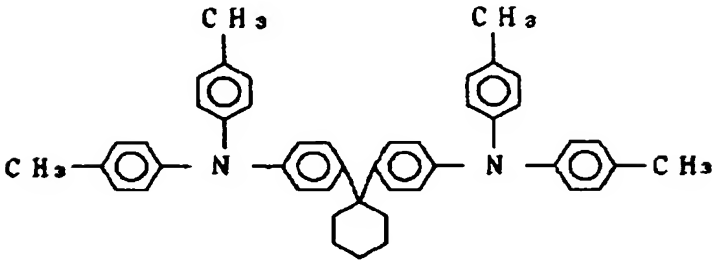
DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the organic thin film light emitting device used as a source of luminescence of various displays, especially relates to the electrode of an organic thin film light emitting device.
[0002]
[Description of the Prior Art] Development and utilization of various display devices are energetically advanced with rapid increase of the need of the flat display which changes to the conventional Braun tube. An electroluminescent element (it considers as an EL element below) is also based on such needs, and attention is attracted with the high resolution and the high visibility it is especially invisible on other displays as a spontaneous light emitting device of all solid-states.
[0003] Current and the thing put in practical use are EL elements which consist of an inorganic material which used the ZnS/Mn system for the luminous layer. However, since the driver voltage required for luminescence of this kind of inorganic EL element is as high as about 200V, the actuation approach becomes complicated and it has the trouble that a manufacturing cost is high. Moreover, since the effectiveness of blue luminescence is low, full-color-izing is difficult. On the other hand, since driver voltage required for luminescence can reduce substantially the thin film light emitting device using an organic material and it fully has the possibility of full-color-izing by addition of various luminescent material, research is activating it in recent years.
[0004] In the structure which carried out the laminating of a hole injection layer and the luminous layer, and vapor-deposited the alloy (mixing ratio 10:1) of Mg and Ag on this on the transparent electrode which consists of an indium-stannic-acid ghost (it omits Following ITO) especially By using tris (8-hydroxyquinoline) aluminum for luminescence material, and using a 1 and 1'-bis(4-N and N-JITORI aminophenyl) cyclohexane for hole-injection material They are 1000 cd/m2 by the direct-current-voltage impression not more than 10V. Since the report that the above brightness was obtained was made, the spur has been applied to development. (Appl.Phys.Lett.51, 913, (1987)) Drawing 3 is the sectional view showing the conventional organic thin film light emitting device. the hole-injection electrode 2 which consists of transparence electric conduction film, such as an indium-stannic-acid ghost (Following ITO is called) and tin oxide, on the insulating transparence substrates 1, such as glass, — subsequently sequential membrane formation of a hole injection layer 3 and the luminous layer 4 is carried out. Finally the alloy of Mg, Ag, or Mg and In is formed as an electronic notes telegram pole 6.
[0005] Drawing 4 is the sectional view showing the organic thin film light emitting device concerning the example from which this invention differs. In order to raise electron injection nature and to raise luminous efficiency, the electronic injection layer 5 is formed. Generally the hole injection layer in these components, a luminous layer, and an electronic injection layer are formed by the resistance heating method. The same is said of an electronic notes telegram pole. This kind of component the plus side of the DC power supply for actuation by connecting a minus side to hole-injection electrodes, such as an ITO electrode, with electronic notes telegram poles, such as Mg/Ag The electron hole poured in from this hole-injection electrode and the electron poured in from this electronic notes telegram pole are considered to emit light by radiation recombination in the luminous layer, and since the impregnation nature to the luminous layer of an electron hole improved especially by installation of a hole injection layer, that by which the extensive improvement of luminous efficiency was made is presumed.
[0006] Thus, although the organic thin film light emitting device has suggested strongly the possibility of low-battery actuation or full-color-izing, it needs to attain much more improvement in effectiveness, and multiple color-ization by amelioration of component structure, development of an organic material, etc. from now on. There is improvement in stability as an important problem turned to utilization on the other hand, and the problem of property degradation accompanying the prolonged actuation which is about 10,000 hours is the hurdle which must be overcome. Moreover, since an organic thin film is 1 micrometer or less, its membrane formation nature is good and it also needs development of an ingredient without the electric defect of a pinhole etc. Development of an organic material that it can furthermore mass-produce from a viewpoint of mass production nature and cheap and amelioration of the component formation approach are also important technical technical problems.
[0007] Examination of a work function is made in order to raise the electron injection nature from an electronic notes telegram pole to an organic layer for an improvement of luminous efficiency. For example, the alloy with which a work function contains a metal 4eV or less is indicated by JP,63-264692,A, JP,63-295695,A, and JP,2-15595,A. Especially, the alloy of Mg and Ag and the alloy of Mg and In are in use, and it was formed in 1000 thru/or the thickness of 3000A.

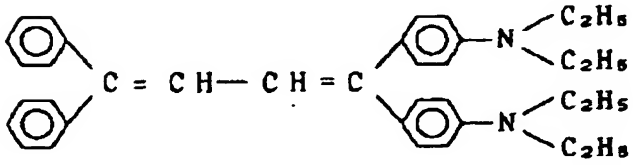
[0008]
[Problem(s) to be Solved by the Invention] However, when the above alloys of Mg and Ag and the alloy of Mg and In were used for an electronic notes telegram pole, there was a phenomenon in which an electronic notes telegram pole exfoliated in the continuation luminescence trial by long duration actuation of a component, and there was a problem that the dependability of a component was low. It is in offering the organic thin film light emitting device which this invention is made in view of an above-mentioned point, and that object prevents exfoliation of an electrode, and is excellent in long-term stability.
[0009]
[Means for Solving the Problem] It is what the above-mentioned object has the electrode of the couple of a hole-injection electrode and an electronic notes telegram pole, and the charge impregnation layer and luminous layer which were inserted into this electrode according to this invention, and a charge impregnation layer receives impregnation of a charge from an electrode, and, subsequently to a luminous layer, carries out transport impregnation of this. It is the thing of the hole injection layer which receives impregnation of an electron hole from a hole-injection electrode, and the electronic injection layers which receive impregnation of an electron from an electronic notes telegram pole which contains a hole injection layer at least. A luminous layer emits light in predetermined wavelength in response to impregnation of an electron hole and an electron, and the electrode of a couple is attained by supposing that an electronic notes telegram pole consists of the impregnation band section and the guard-band section before long.
[0010]
[Function] The guard-band section raises the adhesion of the impregnation band section, and prevents exfoliation of an electronic notes telegram pole.
[0011]
[Example] Next, the example of this invention is explained based on a drawing. Drawing 1 is the sectional view showing the organic thin film light emitting device concerning the example of this invention. Drawing 2 is the sectional view showing the organic thin film light emitting device concerning the example from which this invention differs. 1 — an insulating transparence substrate and 2 — for a luminous layer and 5, as for an electronic notes telegram pole and 61, an electronic injection layer and 6 are [a hole-injection electrode and 3 / a hole injection layer and 4 / the impregnation band section and 62] the guard-band sections.
[0012] The insulating transparence substrate 1 is the base material of an organic thin film light emitting device, and glass, resin, etc. are used. The hole-injection electrode 2 consists of transparence electric conduction film, such as semipermeable membrane, such as gold and nickel, and an indium-stannic-acid ghost (ITO), tin oxide (SnO2), and is formed of resistance heating vacuum evaporationo, electron beam evaporation, a spatter, etc. 100 thru/or the thickness of thickness of 2000A are desirable.
[0013] In the maximal value of the light which conveyed the electron hole, poured into the luminous layer efficiently, and emitted light to it, the thing transparent as much as possible of a hole injection layer 3 is desirable. as the membrane formation approach — a spin coat, casting, and LB — although there are law, resistance heating vacuum evaporationo, electron beam evaporation, etc., resistance heating vacuum evaporationo is common. Thickness is 200 thru/or 5000A and is 300 thru/or 800A suitably. As hole-injection matter, a hydrazone compound, a pyrazoline compound, a stilbene compound, an amine system compound, etc. are used. The typical hole-injection matter is shown in a chemical formula (3-1) thru/or a chemical formula (3-7) below.
[0014]
[Formula 1]



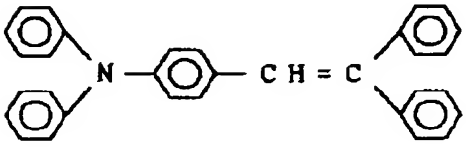
(3 - 1)



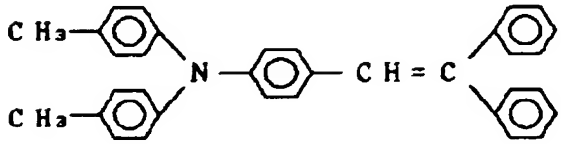
(3 - 2)



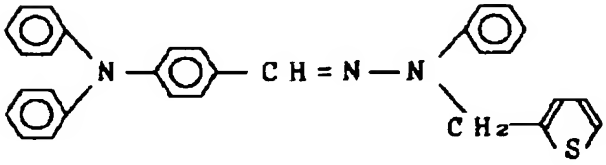
(3 - 3)



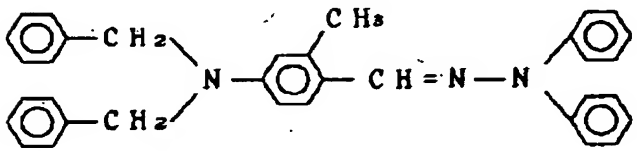
(3 - 4)



(3 - 5)



(3 - 6)

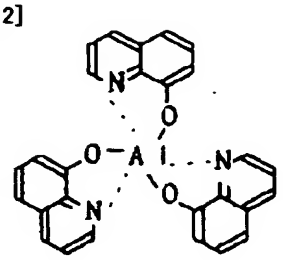


(3 - 7)

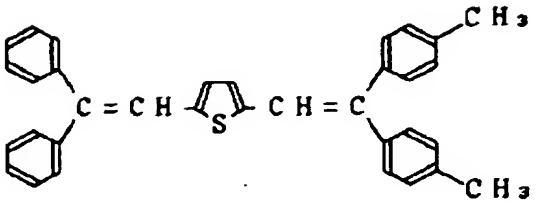
[0015] A luminous layer emits light efficiently with the electron poured in from the electron hole, electronic notes telegram pole, or electronic injection layer poured in from the hole injection layer. as the membrane formation approach — a spin coat, casting, and LB — although there are law, resistance heating vacuum evaporationo, electron beam evaporation, etc., resistance heating vacuum evaporationo is common. Thickness is 200 thru/or 5000A and is 300 thru/or 800A suitably.

[0016] As photogene, metal chelate compound, such as said tris (8-hydroxyquinoline) aluminum, a peri non derivative, a JISUCHIRIRU benzene derivative, etc. are used. Typical photogene is shown in a chemical formula (4-1) thru/or a chemical formula (4-5) below.

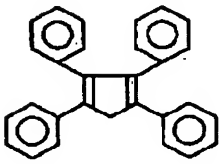
[0017]
[Formula 2]



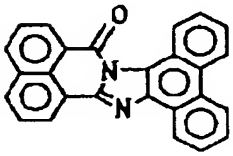
(4 - 1)



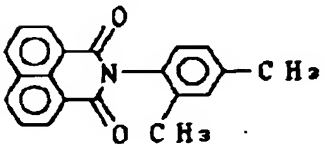
(4 - 2)



(4 - 3)



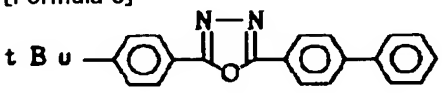
(4 - 4)



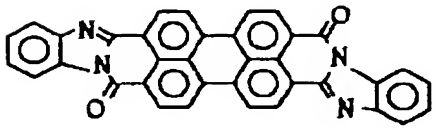
(4 - 5)

[0018] An electronic injection layer needs to convey and pour an electron into a luminous layer efficiently. as the membrane formation approach — a spin coat, casting, and LB — although there are law, resistance heating vacuum evaporationo, electron beam evaporation, etc., resistance heating vacuum evaporationo is common. Thickness is 200 thru/or 5000A and is 300 thru/or 800A suitably. As quality of an electronic notes receptacle, an OKISA diazole derivative, a perylene tetracarboxylic acid derivative, a diphenoquinone series compound, etc. are used. The typical quality of an electronic notes receptacle is shown in a chemical formula (5-1) thru/or a chemical formula (5-3).
[0019] A metal 4eV or less is used for the work function which is excellent in the electron injection nature to the luminous layer or charge impregnation layer of a substrate as the impregnation band section 61 of the electronic notes telegram pole 6 was mentioned above. Mg, In, calcium, Ti, Zr, etc. were the optimal as a result of the detailed experiment. Moreover, about the thickness of the impregnation band section, the remarkable stabilizing effect was obtained within the limits of 30 thru/or 150A. That is, the exfoliation under continuation luminescence trial was brought forward in bigger thickness than 150A, and the impregnation band section was formed in island shape in

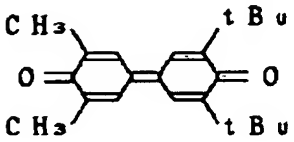
thickness smaller than 30A, and aggravation of the electron injection nature to a substrate layer was caused.
[0020] About the guard-band section of the electronic notes telegram pole 6, with Ag, Au, Cu, aluminum, etc., the good result was obtained and remarkable effectiveness was acquired in 1000A or more of thickness.
[0021]
[Formula 3]



(5 - 1)



(5 - 2)



(5 - 3)

[0022] The glass of 50mm angle which prepared the indium-stannic-acid ghost (ITO) of 2000A of example 1 thickness was used as the substrate, this substrate was laid in resistance heating vacuum evaporationo equipment, and membranes were formed in order of the hole injection layer 3 and the luminous layer 4. On the occasion of membrane formation, the inside of a vacuum tub was decompressed up to 8x10 to 4 Pa. To the hole injection layer, it heated the boat temperature 150 thru/or in 180 degrees C using the hole-injection matter shown in a chemical formula (3-1), and the membrane formation rate was carried out in 2A/s, and was formed 600A. To the luminous layer (8-hydroxyquinoline), it heated the boat temperature 250 thru/or in 350 degrees C using aluminum, and the membrane formation rate was carried out in 2A/s, and was formed 600A. After this, ejection and the stainless steel mask for dot patterns with a diameter of 5mm were attached from resistance heating vacuum evaporationo equipment, the substrate was newly laid in resistance heating vacuum evaporationo equipment, 1000A of 50A of Au (s) was continuously formed as the guard-band section 62 in Mg as the impregnation band section 61, and it considered as the electronic notes telegram pole 6.
The organic thin film light emitting device was created like the example 1 except forming 1000A of Ag as the guard-band section in an example 2 electronic notes telegram pole.
The organic thin film light emitting device was created like the example 1 except forming 1000A of aluminum as the guard-band section in an example 3 electronic notes telegram pole.
The organic thin film light emitting device was created like the example 1 except forming 1000A of example of comparison 1 electronic notes telegram poles using Mg and In (mixing ratio rate 10 to 1).
After forming 2000A of ITO(s) as a hole-injection electrode 2 on the glass substrate 1 of 450mm angle of examples, this ITO substrate was laid in vacuum devices like the example 1, and sequential creation was carried out with the hole injection layer 3, the luminous layer 4, and the electronic injection layer 5. 1000A of guard-band sections which consist of Ag continuously the impregnation band section 61 which becomes the last from Mg as an electronic notes telegram pole 50A was formed. The organic thin film light emitting device was formed like the example 1 using the matter shown with a chemical formula (5-1) as quality of an electronic notes receptacle except forming 400A whenever [boat stoving temperature] by 3A/s in 300 degrees C and membrane formation rate.
The organic thin film light emitting device was created like the example 4 except forming 1000A of example of comparison 2 electronic notes telegram poles using Mg and In (mixing ratio rate 10 to 1). Thus, direct current voltage is impressed to the obtained organic thin film light emitting device, and it is 100 cd/m2. Initial luminous efficiency and initial brightness 100 cd/m2 which can be set The luminescence time amount when performing a continuation luminescence trial is shown in a table 1. All luminescence was green (main wavelength: 550nm) homogeneity luminescence.
[0023]
[A table 1]

	発光効率 (lm/W)	連続発光時間 (h)
実施例1	1．47	1200
実施例2	1．43	1100
実施例3	1．46	1000
比較例1	1．52	150
実施例4	1．67	1150
比較例2	1．73	200

It turns out that the organic thin film light emitting device which formed the electronic notes telegram pole from the guard-band section and the impregnation band section as seen in a table 1 shows remarkable stability in a continuation luminescence trial.

[0024]

[Effect of the Invention] It is what it has the electrode of the couple of a hole-injection electrode and an electronic notes telegram pole, and the charge impregnation layer and luminous layer which were inserted into this electrode according to this invention, and a charge impregnation layer receives impregnation of a charge from an electrode, and, subsequently to a luminous layer, carries out transport impregnation of this. It is the thing of the hole injection layer which receives impregnation of an electron hole from a hole-injection electrode, and the electronic injection layers which receive impregnation of an electron from an electronic notes telegram pole which contains a hole injection layer at least. A luminous layer emits light in predetermined wavelength in response to impregnation of an electron hole and an electron, and before long, since the electrode of a couple consists of the impregnation band section and the guard-band section, an electronic notes telegram pole Adhesion with the impregnation band section and a substrate layer is achieved by the guard-band section, and the organic thin film light emitting device which the exfoliation of an electronic notes telegram pole of is lost as a result, and is excellent in the stability at the time of continuation luminescence is obtained.

[Translation done.]

* NOTICES *

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The sectional view showing the organic thin film light emitting device concerning the example of this invention
[Drawing 2] The sectional view showing the organic thin film light emitting device concerning the example from which this invention differs
[Drawing 3] The sectional view showing the conventional organic thin film light emitting device
[Drawing 4] The sectional view showing the organic thin film light emitting device from which the former differs
[Description of Notations]
1 Insulating Transparence Substrate
2 Hole-Injection Electrode
3 Hole Injection Layer
4 Luminous Layer
5 Electronic Injection Layer
6 Electronic Notes Telegram Pole
61 Impregnation Band Section
62 Guard-Band Section

[Translation done.]

(19)日本国特許庁（ＪＰ）　(12)公開特許公報（Ａ）　(11)特許出願公開番号
特開平5－315078
(43)公開日　平成５年(1993)11月26日

(51)Int.Cl.[5]	識別記号	庁内整理番号	ＦＩ	技術表示箇所
Ｈ０５Ｂ　33/12				

審査請求　未請求　請求項の数４(全　８　頁)

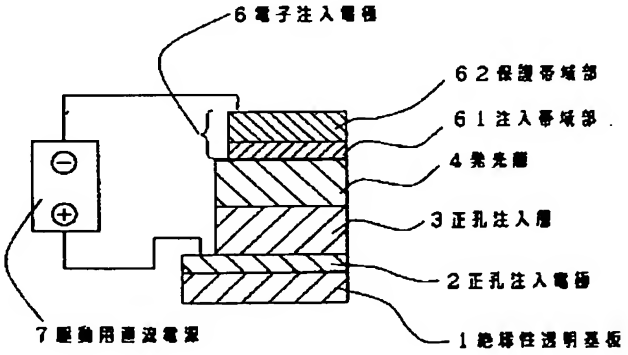
(21)出願番号　特願平4－119339

(22)出願日　平成４年(1992)５月13日

(71)出願人　000005234
富士電機株式会社
神奈川県川崎市川崎区田辺新田１番１号
(72)発明者　鍋田　修
神奈川県川崎市川崎区田辺新田１番１号
富士電機株式会社内
(72)発明者　古庄　昇
神奈川県川崎市川崎区田辺新田１番１号
富士電機株式会社内
(74)代理人　弁理士　山口　巖

(54)【発明の名称】　有機薄膜発光素子

(57)【要約】
【目的】有機薄膜発光素子の連続発光時における安定性を高める。
【構成】電子注入電極６と正孔注入電極２の少なくとも一方の電極を保護帯域部と注入帯域部を積層して形成する。



1

【特許請求の範囲】

【請求項１】正孔注入電極および電子注入電極の一対の電極と、この電極に挟まれた電荷注入層と発光層とを有し、

電荷注入層は電極から電荷の注入を受け、次いでこれを発光層に輸送注入するもので、正孔注入電極から正孔の注入を受ける正孔注入層と電子注入電極から電子の注入を受ける電子注入層のうちの少なくとも正孔注入層を含むものであり、

発光層は正孔と電子の注入を受けて所定の波長の発光を行うものであり、

一対の電極はそのうち電子注入電極が注入帯域部と保護帯域部とからなることを特徴とする有機薄膜発光素子。

【請求項２】請求項１記載の有機薄膜発光素子において、注入帯域部の膜厚が３０ないし１５０Åの範囲にあることを特徴とする有機薄膜発光素子。

【請求項３】請求項１記載の有機薄膜発光素子において、注入帯域部が仕事関数４ｅＶ以下の金属からなることを特徴とする有機薄膜発光素子。

【請求項４】請求項３記載の有機薄膜発光素子において、注入帯域部がマグネシウム金属であることを特徴とする有機薄膜発光素子。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】この発明は各種表示装置の発光源として用いられる有機薄膜発光素子に係り、特に有機薄膜発光素子の電極に関する。

【０００２】

【従来の技術】従来のブラウン管にかわるフラットディスプレイの需要の急増に伴い、各種表示素子の開発及び実用化が精力的に進められている。エレクトロルミネッセンス素子（以下ＥＬ素子とする）もこうしたニーズに即するものであり、特に全固体の自発発光素子として、他のディスプレイにはない高解像度及び高視認性により注目を集めている。

【０００３】現在、実用化されているものは、発光層にＺｎＳ／Ｍｎ系を用いた無機材料からなるＥＬ素子である。しかるに、この種の無機ＥＬ素子は発光に必要な駆動電圧が２００Ｖ程度と高いため駆動方法が複雑となり製造コストが高いといった問題点がある。また、青色発光の効率が低いため、フルカラー化が困難である。これに対して、有機材料を用いた薄膜発光素子は、発光に必要な駆動電圧が大幅に低減でき、かつ各種発光材料の添加によりフルカラー化の可能性を充分に持つことから、近年研究が活発化している。

【０００４】特に、インジウムースズ酸化物（以下ＩＴＯと略する）からなる透明電極上に、正孔注入層と発光層を積層し、この上にＭｇとＡｇの合金（混合比１０：１）を蒸着した構造において、発光材にトリス（８－ヒドロキシキノリン）アルミニウムを、正孔注入材に１，

2

１’－ビス（４－Ｎ，Ｎ－ジトリアミノフェニル）シクロヘキサンを用いることにより、１０Ｖ以下の直流電圧印加で１０００ｃｄ／m^2 以上の輝度が得られたという報告がなされて以来開発に拍車がかけられた。（Appl. Phys. Lett. 51, 913, (1987)）図３は従来の有機薄膜発光素子を示す断面図である。ガラス等の絶縁性透明基板１上にインジウムースズ酸化物（以下ＩＴＯと称する）、酸化スズ等の透明導電膜からなる正孔注入電極２、次いで正孔注入層３、発光層４を順次成膜する。最後に電子注入電極６としてＭｇとＡｇまたはＭｇとＩｎの合金を形成する。

【０００５】図４はこの発明の異なる実施例に係る有機薄膜発光素子を示す断面図である。電子注入性を向上させて発光効率を高めるために電子注入層５が設けられている。これらの素子における正孔注入層、発光層、電子注入層は一般的に抵抗加熱法により形成される。電子注入電極についても同様である。この種の素子は、駆動用直流電源のプラス側をＩＴＯ電極等の正孔注入電極に、マイナス側をＭｇ／Ａｇ等の電子注入電極と接続することにより、該正孔注入電極から注入された正孔と該電子注入電極から注入された電子が発光層中で輻射再結合により発光するものと考えられており、特に正孔注入層の導入により、正孔の発光層への注入性が向上したため発光効率の大幅な改善がなされたものと推定されている。

【０００６】このように有機薄膜発光素子は低電圧駆動やフルカラー化の可能性を強く示唆しているが今後素子構造の改良や有機材料の開発等により一層の効率向上と多色化を図る必要がある。一方実用化に向けての重要課題として安定性の向上があり１万時間程度の長時間駆動に伴う特性劣化の問題は乗り越えなければならないハードルである。また有機薄膜は１μｍ以下であるため成膜性が良好でピンホール等の電気的欠陥のない材料の開発も必要である。さらに量産性の観点から大量生産が可能で安価な有機材料の開発や素子形成方法の改良も重要な技術課題である。

【０００７】発光効率の改善のために電子注入電極から有機層への電子注入性を向上させるべく仕事関数の検討がなされている。例えば特開昭６３－２６４６９２号公報，特開昭６３－２９５６９５号公報，特開平２－１５９５号公報には仕事関数が４ｅＶ以下の金属を含む合金が開示されている。特にＭｇとＡｇの合金，ＭｇとＩｎの合金が主流であり、１０００ないし３０００Åの厚さに形成されていた。

【０００８】

【発明が解決しようとする課題】しかしながら上述のようなＭｇとＡｇの合金，ＭｇとＩｎの合金を電子注入電極に使用した場合、素子の長時間駆動による連続発光試験において電子注入電極が剥離するという現象があり素子の信頼性が低いという問題があった。この発明は上述の点に鑑みてなされその目的は電極の剥離を防止して長

期の安定性に優れる有機薄膜発光素子を提供することにある。

【０００９】

【課題を解決するための手段】上述の目的はこの発明によれば正孔注入電極および電子注入電極の一対の電極と、この電極に挟まれた電荷注入層と発光層とを有し、電荷注入層は電極から電荷の注入を受け、ついでこれを発光層に輸送注入するもので、正孔注入電極から正孔の注入を受ける正孔注入層と電子注入電極から電子の注入を受ける電子注入層のうちの少なくとも正孔注入層を含むものであり、発光層は正孔と電子の注入を受けて所定の波長の発光を行うものであり、一対の電極はそのうち電子注入電極が注入帯域部と保護帯域部とからなるとすることにより達成される。

【００１０】

【作用】保護帯域部が注入帯域部の密着性を高めて電子注入電極の剥離を防止する。

【００１１】

【実施例】次にこの発明の実施例を図面に基づいて説明する。図１はこの発明の実施例に係る有機薄膜発光素子を示す断面図である。図２はこの発明の異なる実施例に係る有機薄膜発光素子を示す断面図である。１は絶縁性

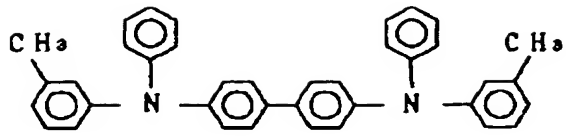
透明基板、２は正孔注入電極、３は正孔注入層、４は発光層、５は電子注入層、６は電子注入電極、６１は注入帯域部、６２は保護帯域部である。

【００１２】絶縁性透明基板１は有機薄膜発光素子の支持体であり、ガラス，樹脂等が用いられる。正孔注入電極２は金，ニッケル等の半透膜やインジウムースズ酸化物（ＩＴＯ），酸化スズ（SnO_2）等の透明導電膜からなり、抵抗加熱蒸着，電子ビーム蒸着，スパッタ法等により形成される。膜厚は１００ないし２０００Åの厚さが好ましい。

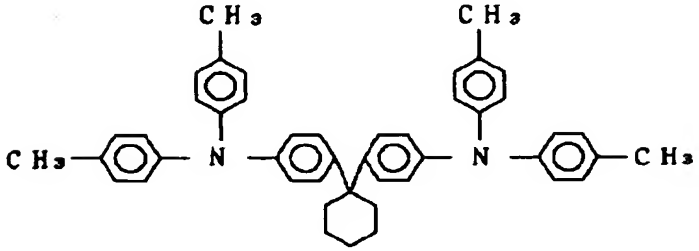
【００１３】正孔注入層３は発光層に効率良く正孔を輸送，注入し発光した光の極大値において出来るだけ透明であることが望ましい。成膜方法としてはスピンコート，キャスティング，ＬＢ法，抵抗加熱蒸着，電子ビーム蒸着等があるが抵抗加熱蒸着が一般的である。膜厚は２００ないし５０００Åであり、好適には３００ないし８００Åである。正孔注入物質としてはヒドラゾン化合物，ピラゾリン化合物，スチルベン化合物，アミン系化合物などが用いられる。代表的な正孔注入物質が以下化学式（３－１）ないし化学式（３－７）に示される。

【００１４】

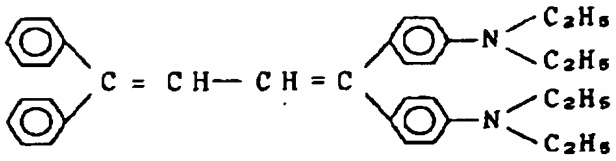
【化１】



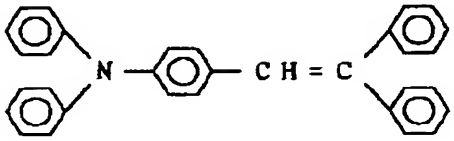
(3-1)



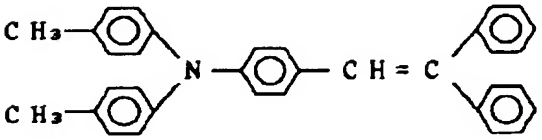
(3-2)



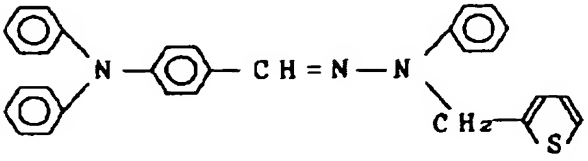
(3-3)



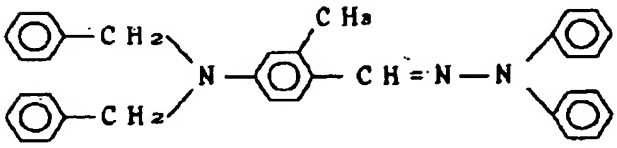
(3-4)



(3-5)



(3-6)



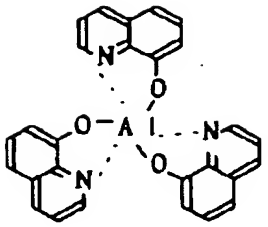
(3-7)

【００１５】発光層は正孔注入層より注入された正孔と電子注入電極または電子注入層から注入された電子により効率良く発光を行う。成膜方法としてはスピンコート，キャスティング，ＬＢ法，抵抗加熱蒸着，電子ビーム蒸着等があるが抵抗加熱蒸着が一般的である。膜厚は２００ないし５０００Åであり、好適には３００ないし８００Åである。

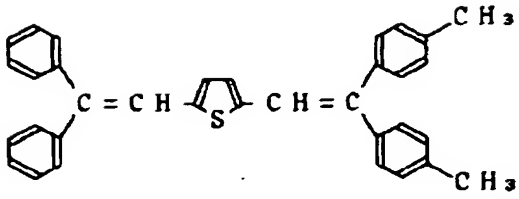
【００１６】発光物質としては前記トリス（８－ヒドロキシキノリン）アルミニウム等の金属キレート化合物やペリノン誘導体，ジスチリルベンゼン誘導体，等が用いられる。代表的な発光物質が以下化学式（４－１）ないし化学式（４－５）に示される。

【００１７】

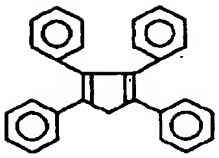
【化２】



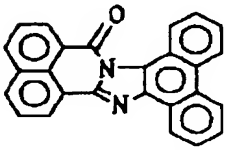
（４－１）



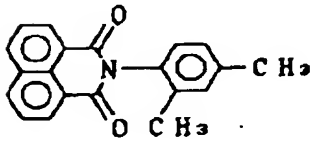
（４－２）



（４－３）



（４－４）



（４－５）

【００１８】電子注入層は電子を発光層に効率良く輸送，注入することが必要である。成膜方法としてはスピンコート，キャスティング，ＬＢ法，抵抗加熱蒸着，電子ビーム蒸着等があるが抵抗加熱蒸着が一般的である。膜厚は２００ないし５０００Åであり、好適には３００ないし８００Åである。電子注入物質としてはオキサジアゾール誘導体，ペリレンテトラカルボン酸誘導体，ジフェノキノン系化合物などが用いられる。代表的な電子注入物質が化学式（５－１）ないし化学式（５－３）に示される。

【００１９】電子注入電極６の注入帯域部６１は前述したように下地の発光層または電荷注入層への電子注入性に優れる仕事関数が４ｅＶ以下の金属が用いられる。詳細な実験の結果Ｍｇ，Ｉｎ，Ｃａ，Ｔｉ，Ｚｒ等が最適であった。また注入帯域部の膜厚については３０ないし１５０Åの範囲内において顕著な安定効果が得られた。即ち１５０Åよりも大きな膜厚においては連続発光試験中の剥離が早まり、また３０Åよりも小さな膜厚においては注入帯域部が島状に形成され下地層への電子注入性の悪化を招いた。

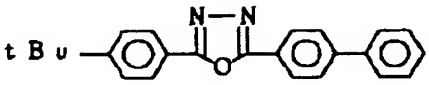
【００２０】電子注入電極６の保護帯域部についてはＡｇ，Ａｕ，Ｃｕ，Ａｌ等で良好な結果が得られ、膜厚１

０００Å以上において顕著な効果が得られた。

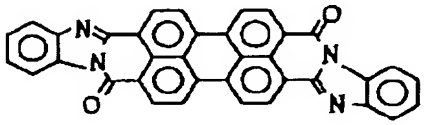
【００２１】

＊【化３】

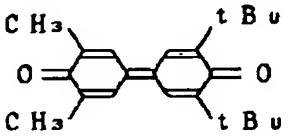
＊



（５－１）



（５－２）



（５－３）

【００２２】実施例１

膜厚２０００Åのインジウムースズ酸化物（ＩＴＯ）を設けた５０mm角のガラスを基板とし、この基板を抵抗加熱蒸着装置内に載置し、正孔注入層３、発光層４の順に成膜した。成膜に際して真空槽内は8×10^{-4} Ｐａまで減圧した。正孔注入層には化学式（３－１）に示される正孔注入物質を用い、ボート温度１５０ないし１８０℃の範囲で加熱し、成膜速度を２Å／ｓとして６００Å形成した。　発光層には（８－ヒドロキシキノリン）アルミニウムを用い、ボート温度２５０ないし３５０℃の範囲で加熱し、成膜速度を２Å／ｓとして６００Å形成した。このあと基板を抵抗加熱蒸着装置から取り出し、直径５mmのドットパターン用ステンレスマスクを取り付け、新たに抵抗加熱蒸着装置内に載置し、注入帯域部６１としてＭｇを５０Å、続いて保護帯域部６２としてＡｕを１０００Å形成し電子注入電極６とした。

実施例２

電子注入電極における保護帯域部としてＡｇを１０００Å形成する以外は実施例１と同様にして有機薄膜発光素子を作成した。

実施例３

電子注入電極における保護帯域部としてＡｌを１０００Å形成する以外は実施例１と同様にして有機薄膜発光素子を作成した。

比較例１

電子注入電極をＭｇとＩｎ（混合比率１０対１）を用いて１０００Å形成する以外は実施例１と同様にして有機薄膜発光素子を作成した。

実施例４

５０mm角のガラス基板１上に正孔注入電極２としてＩＴＯを２０００Å形成したのち、このＩＴＯ基板を実施例１と同様にして真空装置内に載置し、正孔注入層３，発光層４，電子注入層５と順次作成した。最後に電子注入電極としてＭｇからなる注入帯域部６１を５０Å、続いてＡｇからなる保護帯域部を１０００Å形成した。電子注入物質として化学式（５－１）で示される物質を用い、ボート加熱温度３００℃、成膜速度３Å／ｓにて４００Å形成する以外は実施例１と同様にして有機薄膜発光素子を形成した。

比較例２

電子注入電極をＭｇとＩｎ（混合比率１０対１）を用いて１０００Å形成する以外は実施例４と同様にして有機薄膜発光素子を作成した。このようにして得られた有機薄膜発光素子に直流電圧を印加し、１００ｃｄ／m^2 における初期発光効率と初期輝度１００ｃｄ／m^2 にて連続発光試験を行ったときの発光時間を表１に示す。発光は全て緑色（中心波長：５５０ｎｍ）の均一発光であった。

【００２３】

【表１】

	発光効率（lm／W）	連続発光時間（h）
実施例１	１．４７	１２００
実施例２	１．４３	１１００
実施例３	１．４６	１０００
比較例１	１．５２	１５０
実施例４	１．６７	１１５０
比較例２	１．７３	２００

表１に見られるように電子注入電極を保護帯域部と注入帯域部とから形成した有機薄膜発光素子は連続発光試験において顕著な安定性を示すことがわかる。

【００２４】

【発明の効果】この発明によれば正孔注入電極および電子注入電極の一対の電極と、この電極に挟まれた電荷注入層と発光層とを有し、電荷注入層は電極から電荷の注入を受け、次いでこれを発光層に輸送注入するもので、正孔注入電極から正孔の注入を受ける正孔注入層と電子注入電極から電子の注入を受ける電子注入層のうちの少なくとも正孔注入層を含むものであり、発光層は正孔と電子の注入を受けて所定の波長の発光を行うものであり、一対の電極はそのうち電子注入電極が注入帯域部と保護帯域部とからなるので、保護帯域部により注入帯域部と下地層との密着が図られ、その結果電子注入電極の剥離がなくなって連続発光時の安定性に優れる有機薄膜発光素子が得られる。

＊【図面の簡単な説明】

【図１】この発明の実施例に係る有機薄膜発光素子を示す断面図

【図２】この発明の異なる実施例に係る有機薄膜発光素子を示す断面図

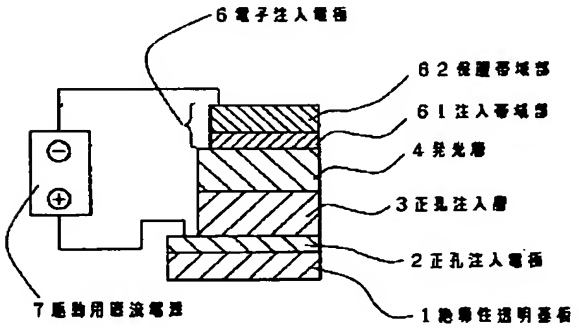
【図３】従来の有機薄膜発光素子を示す断面図

【図４】従来の異なる有機薄膜発光素子を示す断面図

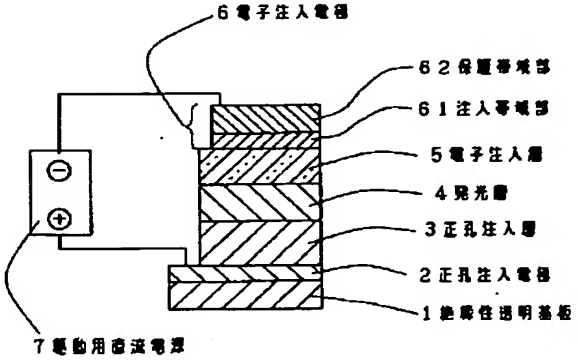
【符号の説明】

１　絶縁性透明基板
２　正孔注入電極
３　正孔注入層
４　発光層
５　電子注入層
６　電子注入電極
６１　注入帯域部
６２　保護帯域部

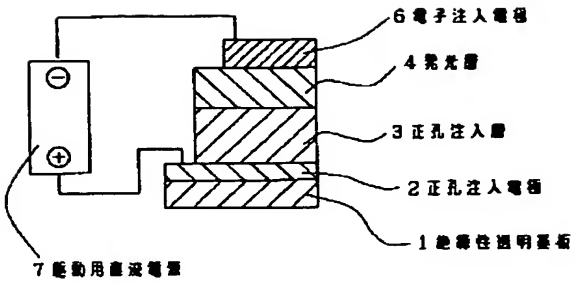
【図１】



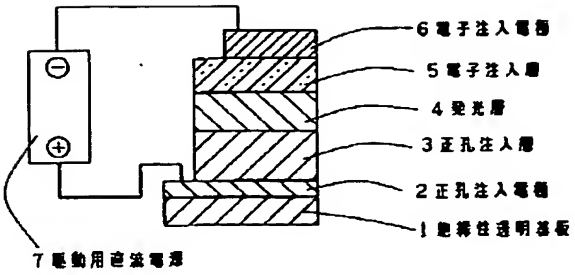
【図２】



【図３】


６電子注入電極
４発光層
３正孔注入層
２正孔注入電極
１絶縁性透明基板
７駆動用直流電源

【図４】


６電子注入電極
５電子注入層
４発光層
３正孔注入層
２正孔注入電極
１絶縁性透明基板
７駆動用直流電源